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## Atomic Layer Deposition of ZnO in Quantum Dot Thin Films\*\*

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Atomic layer deposition (ALD) is a useful thin-film growth method that relies on self-limiting chemical reactions between vapors of alternating precursors and a solid surface.<sup>[1]</sup> Gaseous diffusion of the ALD precursor molecules ensures that the deposition is conformal and uniform in thickness, even when the substrate has a complex topography.<sup>[2]</sup> The past few decades have also seen much developments in colloidal synthesis, where highly monodisperse colloidal nanoparticles of sizes between 2 and 10 nm and of many different materials can be prepared and assembled into thin films.<sup>[3,4]</sup> These particles present potential applications ranging from phosphors to photovoltaics, and can be employed in basic research of designer materials.<sup>[3]</sup>

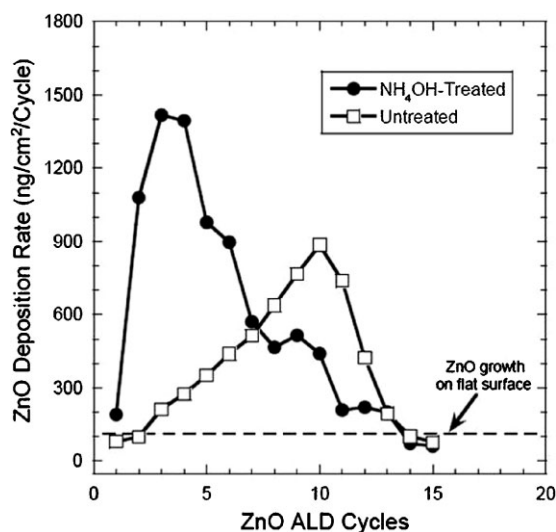
Nanocrystal films are well suited for ALD, since their open structure allows diffusion of gaseous precursors, and thus allows an easy layer-by-layer filling of interstices. Furthermore, pore sizes of the order of a few nanometers suggest that complete infiltration and filling should take place after only a few monolayers, indicating that this method could also be cost-effective.

In this work, we apply ALD to films of nanocrystals, using ZnO to infiltrate colloidal CdSe and core/shell quantum-dot films. The dots were prepared according to previously described methods,<sup>[3]</sup> and films of dots with thicknesses of 50–100 nm were prepared by drop-casting.<sup>[3]</sup> ZnO ALD was performed in two separate instruments, using alternating exposures to diethyl zinc (Strem) and deionized water (partial pressures  $\sim 133.3$  Pa, 1–50 s duration, at 100 °C). One system comprises a cold-walled quartz chamber with an internal resistive sample heater, optical access, and in situ current measurement with resolution  $\sim 10$  pA. The second system is a hot-walled stainless steel tube with an in situ quartz crystal microbalance (QCM)<sup>[5]</sup> and optical access for photoluminescence measurements. Both ALD systems yielded similar results.

To evaluate the extent of infiltration by the ZnO after ALD, CdSe nanocrystal films ( $\sim 50$  nm thickness) were drop-cast onto

quartz sensors that were then used for in situ QCM measurements (Fig. 1, open squares). In these dried films, the initial ZnO ALD mass uptake is close to  $113 \text{ ng cm}^{-2} \text{ cycle}^{-1}$ , the value measured for a clean sensor.<sup>[6]</sup> The uptake increases slowly in subsequent cycles, indicating only modest infiltration. This behavior is expected, since these dried films contain a large fraction of long-hydrocarbon-chain ligands that could block the interstitial voids and also inhibit nucleation of ZnO ALD.<sup>[7]</sup> For effective infiltration, the surfaces and voids must be clear and the surface must react with the ALD precursors. To improve infiltration, we treated the films with 3% by weight aqueous ammonium hydroxide (30%) in ethanol. Following a 60 s  $\text{NH}_4\text{OH}$  treatment, infrared spectroscopy measurements revealed an 80–90% reduction of the CH band intensity, along with an increased NH/OH contribution. Ellipsometry showed that the ligand removal shrinks the film thickness by  $\sim 30\%$ , and increases the optical dielectric constant by  $\sim 10\%$ .

For films of CdSe dots that have been treated with  $\text{NH}_4\text{OH}$ , the ZnO ALD leads to faster, higher mass uptake, of up to  $1400 \text{ ng cm}^{-2} \text{ cycle}^{-1}$ , which is equivalent to 13 ZnO layers



**Figure 1.** QCM measurements of the mass deposited during 15 cycles of ZnO ALD on sensors that had been previously coated with CdSe quantum dot films. The dashed line shows the ZnO growth rate, measured on a smooth QCM sensor with no film. The much larger growth rates measured for the CdSe films demonstrate infiltration of the porous matrix by the ZnO ALD precursors. ZnO ALD occurs promptly on the film that had been treated with  $\text{NH}_4\text{OH}$  (solid circles). In contrast, ZnO nucleation is delayed on an untreated film (open squares).

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(Fig. 1, solid circles), or  $13\times$  larger than for the flat surface. This uptake decreases after a few cycles.

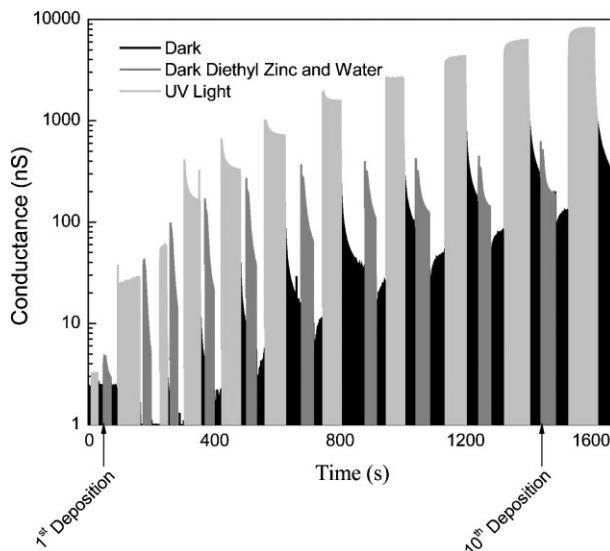
The maximum possible uptake is estimated using the surface area of a film of thickness  $d$  containing spheres of radius  $R$  at a volume fraction  $\Phi$ , relative to the flat area  $A$ . Considering the sphere surface,  $4\pi R^2$ , and the number of spheres in the film of flat area  $A$  and thickness  $d$ ,  $Ad\Phi/(\frac{4}{3}\pi R^3)$ , the relative surface area is  $3\Phi d/R$ . Assuming a random-close packed fraction of  $\Phi=0.64$ , a 50 nm thick film made of 2.5 nm radius particles should have an uptake of  $\sim 40\times$  more than for a flat surface. The measured uptake of  $13\times$  is significantly smaller than this upper estimate. This may be due to the presence of inaccessible surfaces, or to delayed nucleation on the nanocrystal surfaces, however it confirms a considerable degree of infiltration.

Early studies of CdSe quantum dot films showed they were very insulating, yet photoconductive at high fields ( $10\text{ V }\mu\text{m}^{-1}$ ), with mobilities of  $\sim 10^{-6}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  with slow responses.<sup>[8,9]</sup> A ligand-exchange procedure was shown to dramatically increase this conductivity, with mobilities as high as  $10^{-2}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  in negatively charged films.<sup>[10]</sup> In uncharged films, ligand exchange also improves the photosensitivity. However, the reported mobilities remained low ( $\sim 10^{-5}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ),<sup>[11]</sup> with frequency responses below  $\sim 50\text{ kHz}$ ,<sup>[12]</sup> leaving much room for improvement.

As stated above, ZnO is a good option for improving electron transfer between quantum dots, since it is an n-type conductor. Its bulk conduction-band edge is below that of bulk CdSe, so electrons can easily tunnel between dots, and may even be extracted into the ZnO matrix. Furthermore, although ZnO has a strong tendency to trap holes, its ability to conduct electrons is remarkably resilient to disorder and defects, and should not be affected by the residual hydroxyl groups typically observed in ALD films deposited at low temperatures.<sup>[13]</sup>

The photoconductivity of films of colloidal quantum dots drop-cast on a set of interdigitated electrodes (50 sets of Pt electrodes 5 mm long, 5  $\mu\text{m}$  wide, and 5  $\mu\text{m}$  separation on glass, Abtech Scientific) was measured. In situ photoconductivity measurements at  $100^\circ\text{C}$  under 1 Torr (133.3 Pa) nitrogen reveal significant changes in the photosensitivity with deposited ZnO. As shown in Figure 2, for a CdSe/CdS sample the photoconductance increases by two orders of magnitude with the first three cycles, and then increases more slowly. The dark current, which is initially in the pico Ampere range, increases after the third ZnO cycle. These results suggest that the first few ZnO cycles build  $\text{ZnO}_x$  bridges between the dots, while subsequent cycles increase the ZnO matrix connectivity. In the first few cycles, exposure to diethyl zinc increases the photoconductance and dark conductance (Fig. 2), while exposure to water reduces both, leaving a net increase of  $\sim 5$ – $10$ -fold per cycle for the photoconductance. For a sample that had been exposed to 10 ZnO ALD cycles, increasing the temperature from  $20^\circ\text{C}$  to  $250^\circ\text{C}$  leads to a reversible increase in dark conductance of three orders of magnitude.

Exposure to air reduces both the photoconductivity and dark conductivity by one to two orders of magnitude, leaving a stable net increase of the photoconductivity over the  $\text{NH}_4\text{OH}$

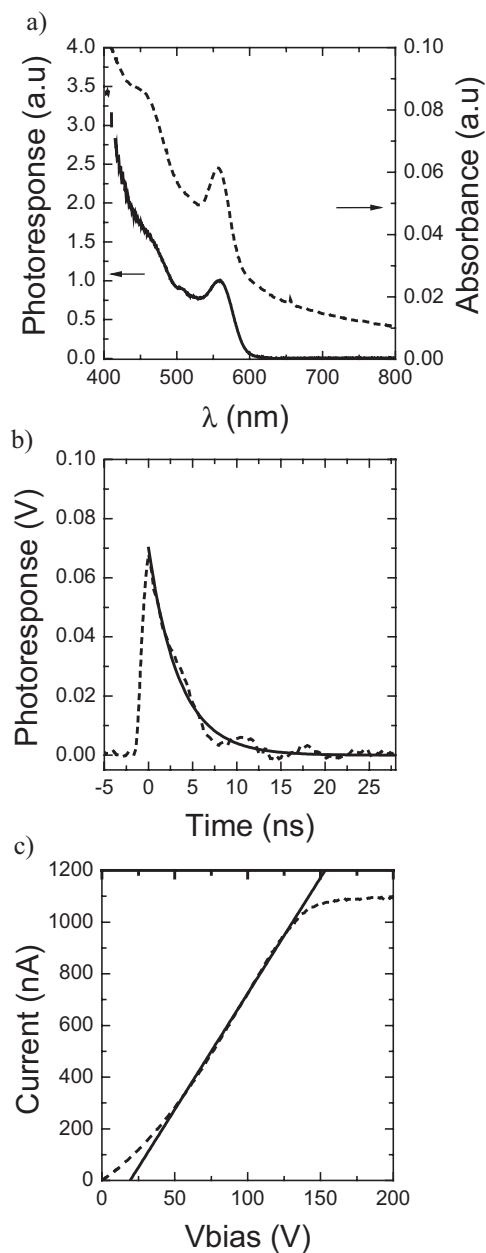


**Figure 2.** Conductance of a CdSe/CdS sample measured in situ at  $100^\circ\text{C}$  during 10 ZnO ALD cycles. Black regions show the dark current measured during the purge portions of the cycles. Dark grey areas show the dark current beginning with exposure to diethyl zinc and finishing with exposure to water. Light grey regions show the current measured under 400 nm illumination.

treated film of 20–100-fold, both for CdSe quantum dots and CdSe/CdS core/shells.

Strong temperature dependence of the dark current, and sensitivity to gas exposures and illumination have been reported for amorphous and polycrystalline semiconductors, such as  $\text{InO}_x$ .<sup>[14]</sup> These observations most likely reflect the ease with which small changes of the local oxidation state can affect the conductivity of these oxides. Here, the very large current increase upon exposure to diethyl zinc is probably a result of partial electron donation by the  $-\text{O}-\text{Zn}-\text{ethyl}$  surface species.

The measurements show that much of the increase in photoconductivity occurs within the first three cycles, while the dark conductivity remains low ( $<10\text{ pA}$  at  $1.5\text{ V}$ ). We then studied the photoresponse in more detail. Figure 3a shows the spectral photoresponse of a  $\sim 3.5\text{ nm}$  CdSe sample, exposed to only three ZnO cycles. It nicely follows the optical absorption behaviour of a film of the same dots prepared on glass and subjected to the same treatment. Besides the photosensitivity increase, the deposited ZnO maintains a fast photoresponse time. With a  $10^5\text{ V A}^{-1}$  amplifier, the response time is  $\sim 1\text{ }\mu\text{s}$ , limited by the amplifier. As shown in Figure 3b, the unamplified response to an 8 ps, 532 nm laser pulse recorded with a 2 GHz oscilloscope is much faster, with a sub-nanosecond rise time and a fall time of  $\sim 3.5\text{ ns}$ . This is 3–4 orders of magnitude faster than previously reported results.<sup>[12]</sup> The fast response implies that electrons rapidly recombine with holes or are trapped. Nevertheless, the improved photosensitivity also implies a relatively high mobility. Assuming that the electron is the single mobile carrier, the primary current is given by  $I = \tau\mu VL^{-2}\eta\alpha eF$ , where  $e$  is the electron charge,  $\tau$  is the electron lifetime (3.5 ns),  $\mu$  is the mobility,  $\eta$  is the carrier



**Figure 3.** a) Photoresponse (solid black line) at 1.5 V bias as a function of optical wavelength. The sample is a CdSe-quantum-dot film exposed to three ZnO cycles. All measurements were performed in air. The dashed line is the absorption spectrum of a quantum dot film on a glass slide, following identical treatment, with a clean slide as the background. The film is optically clear and the rising slope above the exciton wavelength is due to increased reflectivity. b) Response to an 8 ps 532 nm laser pulse measured with a 50  $\Omega$  load and a 2 GHz storage oscilloscope. The dashed line is a 3.5 ns exponential decay. c) Photocurrent versus voltage. The slope of the linear region (solid line) is 9 nA V<sup>-1</sup>.

generation probability per exciton,  $\alpha$  is the absorption,  $L$  is the electrode gap (5  $\mu$ m),  $V$  is the applied bias, and  $F$  is the incident photon flux. At 532 nm, the responsivity, current divided by incident power, of the sample in Figure 3, was 5.7  $\mu$ A W<sup>-1</sup> with

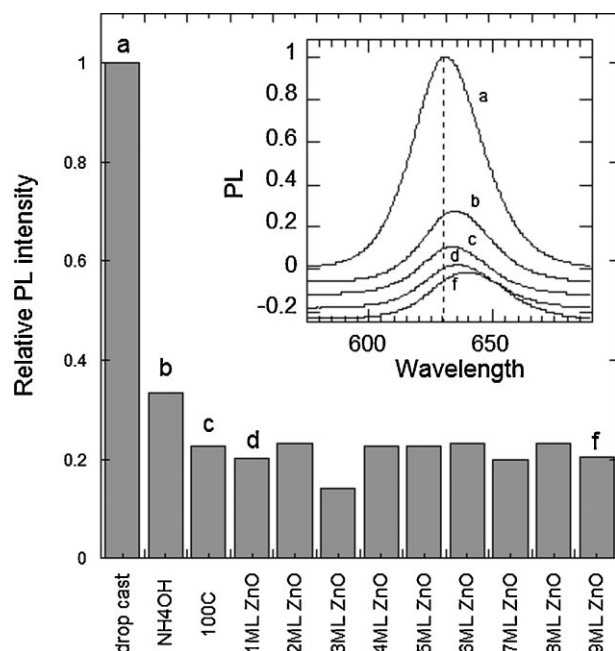
a 1 V bias. The film absorption was  $\sim 10\%$ . Assuming  $\eta = 1$ , the mobility is  $8.7 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This is a lower limit, since  $\eta$  may be less than 1. At 100 V bias, the sensitivity increases three-fold, giving a mobility of  $\sim 2.6 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. An independent determination of the mobility is obtained from the  $I$ - $V$  curve<sup>[11]</sup> shown in Figure 3c. The saturation current,  $I_{\text{sat}}$ , corresponds to  $\tau\mu VL^{-2} = 1$  such that  $I_{\text{sat}} = \eta\alpha eF$ . Assuming that  $\eta = 1$  in the linear and the saturation regimes, the slope of  $I/I_{\text{sat}}$  in the linear regime is  $\tau\mu L^{-2}$ , which gives  $\tau\mu = 2 \times 10^{-9}$  cm<sup>2</sup> V<sup>-1</sup>, and a mobility of  $6 \times 10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

The mobilities estimated in two independent ways are thus in fair agreement, in the  $10^{-2}$ – $10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> range. This is 2–3 orders of magnitude higher than previous mobilities measured from photoconductivity,<sup>[11,12]</sup> and of the order of the highest value observed for n-type CdSe quantum dot films.<sup>[10]</sup> The improved mobility may be due to easier tunneling between dots through the ZnO<sub>x</sub> barriers, or could be due to the improved conductivity of a percolating ZnO<sub>x</sub> matrix. Since the improvement is most significant for the earliest exposure, and arises before significant dark current sets in, we favor the former explanation.

ALD also modifies the optical properties of the quantum dot films. After the NH<sub>4</sub>OH treatment and ALD of ZnO, the index of refraction of the CdSe quantum dot film increases from  $n \sim 1.75$  to  $n \sim 2$  as voids ( $n = 1$ ) become partially filled with the high-index ZnO ( $n = 2.0$ ). One useful property of colloidal quantum dots is their photoluminescence (PL). It was found that both ZnO ALD and Al<sub>2</sub>O<sub>3</sub> ALD (performed using alternating exposures to trimethylaluminum and water) lead to a complete quenching of the luminescence of CdSe quantum dots after several cycles. In situ measurements show that the PL decreases dramatically upon diethyl zinc exposure, but partially recovers after each H<sub>2</sub>O exposure. This may be related to the previously discussed large increase of dark conductivity, and partial electron transfer. In agreement with the hypothesis of electron transfer, CdSe/CdS quantum-dot films lose their PL upon ZnO ALD at  $\sim 100^\circ\text{C}$ . Electron-confining core/shell quantum dots, CdSe/ZnS, are thus better candidates to preserve PL. For these samples, the most damaging processes are the NH<sub>4</sub>OH treatment and  $100^\circ\text{C}$  heating, which together decreased the PL by 75% (Fig. 4). The lower PL efficiency of close-packed films is typically attributed to increased energy transfer between dots. However, as shown in Figure 4, the ZnO ALD did not lead to further decline of the PL. Further studies with optimized nanocrystals as starting materials and a more appropriate ALD material, e.g., ZnS, could lead to robust phosphors.

An added benefit of ZnO ALD is the improvement in the mechanical properties of nanocrystal films. While nanocrystal films can be wiped off a glass substrate before or after NH<sub>4</sub>OH treatment, the ALD-processed films must be removed by acid dissolution.

In summary, ALD is a promising approach to the modification of the properties of close-packed nanocrystal assemblies. Following treatment with dilute ammonia to remove organic impurities, ZnO ALD was shown to successfully



**Figure 4.** Effect of film treatment on the PL of bright CdSe/CdS/ZnS quantum dot films. The peak PL intensity shown by the vertical bars is strongly reduced by the NH<sub>4</sub>OH treatment, as well as by the 100 °C annealing in vacuum. However, subsequent ZnO ALD cycles do not further deteriorate the PL. The inset shows the PL spectra labeled and vertically offset.

infiltrate and advantageously modify CdSe quantum dot films. Retention of PL for cores with a ZnS electron confining shell was demonstrated. ALD on CdSe and CdSe/CdS much improved the photosensitivity, while providing a nanosecond photoresponse. This was due to improvements in mobility by 2–3 orders of magnitude, and is attributed to more facile

electron transfer. These improvements are obtained with only a few ALD cycles, as expected due to the small void sizes. ALD in quantum dot solids can be advantageous in applications such as photovoltaics and light-emitting diodes. Furthermore, ALD of metallic or magnetic materials into other types of nanocrystal solids might also prove beneficial.

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